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Theoretical Determination of the Heats of Formation of Prospective Strained-Ring Rocket Fuels

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ABSTRACT

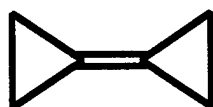
The gas-phase heats of formation of seven unusual strained and substituted organic molecules ranging in size from C_6H_8 to $C_{17}H_{24}N_4O_8$ have been determined using the parallel version of the GAMESS quantum chemistry code. Molecular energies obtained by a number of methods, ranging from the semi-empirical through Hartree-Fock, 6-31(d) geometry optimization and force-constant evaluation with MP2, 6-31(d) single-point energy calculation, have been combined with experimental information to provide the necessary composite thermodynamic parameters. In addition, a variety of resource-tailored strategies for employing these values, some relying upon investigation of the target compound alone and others involving suitable isodesmic reactions, have been critically evaluated and compared with results obtained from the wholly empirical Benson additivity rules. Within the present set of reference molecules, this computation-free approach compares favorably with all but the highest level theoretical treatments.

A. Introduction

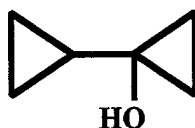
As a measure of the intrinsic energy content of a substance, the standard enthalpy of formation, the energy required for its formation from the elements in their standard states under conventional thermodynamic conditions, constitutes a critical parameter for the evaluation of a candidate propellant's likely performance. Since chemical synthesis of even small quantities of novel chemical compounds can be extremely resource intensive, it is desirable to narrow the search for new materials to only those candidates which show particular promise. In order to be of use to propellant chemists, theoretical predictions of molecular heats of formation must meet the often conflicting criteria of timeliness, affordability, and accuracy. Thus, when encountering a set of perhaps rather speculative proposed fuels, a rapid and approximate preliminary screening procedure might be productively employed in advance of initial experimental investigations and more extensive, and presumably more accurate, theoretical treatments. To these ends the research reported herein is not merely motivated by the quest for the heats of formation of a few specific molecules of present interest but, with a view toward future needs, also gives particular emphasis to evaluating and comparing a variety of established, progressively more expensive theoretical methods within a diverse set of strained molecules of the sort of interest as high-energy propellants.

Specifically, this work reports results of calculations of the ideal-gas enthalpies of formation, $\Delta H_f^\dagger \equiv \Delta H_{f, id\ gas}^{298\ K}$, of the following seven compounds made

or proposed by synthetic chemists in the Propulsion Sciences Division of the Propulsion Directorate, Air Force Research Laboratory.



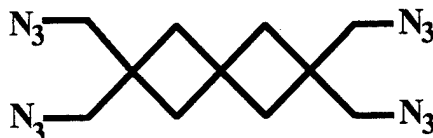
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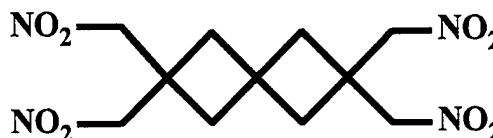
2: 1-cyclopropyl-cyclopropan-1-ol



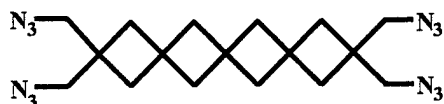
3: 2,6-dioxaspiro[3.3]heptane



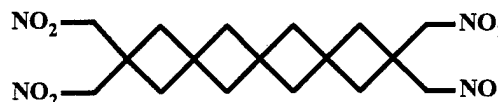
4: 2,2,6,6-tetra(azidomethyl)-spiro[3.3]heptane



5: 2,2,6,6-tetra(nitromethyl)-spiro[3.3]heptane



6: Higher spiro analogue of 4



7: Higher spiro analogue of 5

In addition, the specific impulse, a parameter derived from the enthalpy of formation and more directly indicative of the performance of a molecule in a rocket application, is reported for each.

B. Theoretical Methods for the Calculation of Heats of Formation

There follows a brief survey of some of the more common methods devised for the prediction of molecular heats of formation. A more complete account is provided in a subsequent publication.¹ These approaches may be broadly classified in a number of ways; for present purposes, they are discriminated according to their methodological nature or scope as well as by the more practical criteria of the expense of the calculations which supply their requisite composite parameters.

1. Broad Methodological Classes

Two criteria may be used to classify the methodology of a determination of the molecular heat of formation. First of all, some approaches involve characterization of only the molecule of primary interest (hereafter the "target molecule"), in contrast to those to be discussed subsequently, which seek some cancelation of errors by utilizing the change in energy of a reacting set of molecules.

Of the single-molecule methods considered here, the second criterion, that of additivity, can be employed to further discriminate between those which rely upon the approximate transferability of energetic contributions of chemical moieties such as atoms, bonds, or functional groups (hereafter labeled as *ab lateribus* (literally "from the bricks")) and those which conceive of molecules as complete, fully interacted systems, indivisible to the level of fundamental quantum-chemical

¹ J.D. Mills, *Technical Report*, in preparation.

particles ("single-whole-molecule" approaches). In these latter methods, the calculated quantum-chemical molecular energy, that is, the energy of interaction of the composite electrons and nuclei, may differ from the enthalpy of formation, referenced to the energies of the elements, by several orders of magnitude. Therefore it is common to adjust the molecular energies by a variety of means in order to correct relatively small errors, either in conjunction with or in advance of incorporation of elemental energies and thermodynamic effects.

An alternative means of correcting minor errors in whole-molecule energies is to broaden the calculation to include a group of well-characterized reacting compounds containing, in some sense, similar chemical environments or groups ("reaction-based" approaches) and to take advantage thereby of a partial cancellation of errors between the calculated energies of fully interacted reactants and products. These approaches then separately include the thermodynamic effects of non-zero temperature.

As ordered here, the methods become generally more complicated and, other things being equal, are expected to be more accurate. They also, however, become progressively more subjective, as for example in the selection of the most appropriate reaction between "most similar" reactants and products. Each of the three classes already described are more definitively characterized by the following formulae.

a. Class A-*Ab Lateribus* Methods

The enthalpy of formation of the target molecule may be composed as a simple sum of the combined energetic and thermodynamic contributions of composite chemical groups as:

$$\Delta H_f^\dagger = \sum_{j, \text{groups}} \Delta H_{f,j} \quad (1)$$

where the groups may be operationally defined in a number of ways so as to ensure maximum accuracy and transferability between different molecules.

b. Class B-Additively Corrected Single-Whole-Molecule Methods

Within this work, methods limited to the fully interacted target combine whole-molecule energies with additivity-based corrections, as:

$$\Delta H_f^\dagger = E_{\text{mol}} + \sum_{j, \text{groups}} \Delta H_j \quad (2)$$

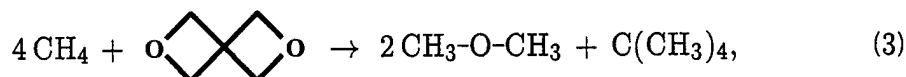
somewhat in the spirit of *ab lateribus* approaches. These undifferentiated adjustments are designed to incorporate thermodynamic effects as well as ameliorate calculational deficiencies.

c. Class C-Reaction-Based Methods

In the present research isodesmic or "bond-preserving" reactions, those in which there are the same number and type of formal bonds in the sets of reactants and products,² are used to determine molecular heats of formation from

² W.J. Hehre, R. Ditchfield, L. Radom, and J.A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

calculated reaction energies. The procedure by which this is effected is perhaps best illustrated with a specific example. The third target compound, 2,6-dioxaspiro[3.3]heptane, could be isodesmically deconstructed as:



the corresponding reactions for the remaining target molecules being suggested by the list of "non-target" or isodesmic-partner compounds listed in Table (D). For each target molecule, the ideal-gas enthalpy of formation is then constructed from:

$$\Delta H_f^\dagger = \Delta(\Delta H_f'^\dagger) - [\Delta E_{\text{eq}} + \Delta E_{\text{zp}} + \Delta(H_{298\text{K}} - H_{0\text{K}})] \quad (4)$$

where each component is defined below, first in general notation, and then, as seems illuminating, in application to the example reaction. The first parameter:

$$\begin{aligned} \Delta(\Delta H_f'^\dagger) &\equiv \sum_{\substack{i', \text{ molecules,} \\ \text{not target}}} \nu_{i'} \Delta H_f'^\dagger(i') \\ &= 2 \Delta H_f^\dagger(\text{CH}_3\text{-O-CH}_3) + \Delta H_f^\dagger(\text{C}(\text{CH}_3)_4) - 4 \Delta H_f^\dagger(\text{CH}_4) \end{aligned} \quad (5)$$

is just the stoichiometrically weighted difference of known heats of formation of all molecules in the reaction except the target. The quantity enclosed in square brackets in equation (4) is just the standard-temperature reaction enthalpy and is composed of three parts:

$$\begin{aligned} \Delta E_{\text{eq}} &\equiv \sum_{i, \text{ molec.}} \nu_i E_{\text{eq}}(i) \\ &= 2 E_{\text{eq}}(\text{CH}_3\text{-O-CH}_3) + E_{\text{eq}}(\text{C}(\text{CH}_3)_4) - 4 E_{\text{eq}}(\text{CH}_4) - E_{\text{eq}}(\text{O} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{O}) \\ \Delta E_{\text{zp}} &\equiv \sum_{i, \text{ molec.}} \nu_i E_{\text{zp}}(i) \\ \Delta(H_{298\text{K}} - H_{0\text{K}}) &\equiv \sum_{i, \text{ molec.}} \nu_i (H_{298\text{K}}(i) - H_{0\text{K}}(i)) \end{aligned} \quad (6)$$

which are similar differences, this time including all participants in the reaction, of, respectively, the energies of the molecules at their theoretical equilibrium geometries, shifts due to zero-point energy, and the "heat capacity correction" which incorporates the enthalpic effects of the standard temperature. To the extent that the structural environments are similar on both sides of the reaction and errors in a calculation are similar for any given type of environment, much of any error is expected to cancel in the indicated differences.

2. Calculational Method

Within each methodological class, specific approaches can be further divided according to the means employed to supply the parameters just described. In the interests of determining the relative value of each method in a resource-limited environment, it seems appropriate to organize the approaches in terms of their computational expense. Therefore, labels indicating the final step in a

Table (A)	
Calculation Type by Computational Expense	
Label	Terminal Calculation Step
I	No computation
II	Semi-Empirical Geometry Optimization and Hessian
III	Hartree-Fock Geometry Optimization
IV	Hartree-Fock Hessian at Minimum Energy Geometry
V	MP2 Energy at HF Optimum Geometry

succession of calculations (Table (A)) will be used hereafter, in addition to the methodological class index already described, to delineate each specific approach; in the same context, the label, Exp, will be used to denote an experimental value.

For the computations performed for this study, the semi-empirical calculations, although involving the same effort as their more sophisticated counterparts to specify the geometry and prepare the input files, consumed negligible computer time. In contrast, each succeeding step (III-V) described in Table (A) was found to require a significant and roughly comparable additional expenditure of resources.

3. Details of Present Methods

a. Method IA-Benson Group Additivity

Although a number of computation-free, *ab lateribus* methods have been devised, this work considers only the most common, the Benson group-additivity prescription.³ Based wholly upon comparison with experiment, representative enthalpic contributions of chemical groups, each generally a single atom discriminated according to its bonding partners, have been tabulated and may be quite readily applied to many molecules with classical chemical structures.

b. IIB Methods-Semi-Empirical Values

A number of computational codes directly report semi-empirical enthalpies of formation after shifting the fully interacted molecular energy by atom-based adjustments derived from experimental and theoretical considerations.⁴ Results of this type are denoted hereafter with the label IIB followed by a parenthetical indication of the semi-empirical Hamiltonian used.

c. Method IIIB-Ibrahim/Schleyer Hartree-Fock Atom Equivalents

Similarly, Ibrahim and Schleyer,⁵ within a reference set of molecules for which accurate experimental values are known, found an optimum set of atom-based shifts which yield heats of formation from the total, Hartree-Fock molecular energy. These factors subsume energetic and thermodynamic effects, as well as corrections for computational deficiencies.

³ S.W. Benson, *Thermochemical Kinetics*, Second Ed., (Wiley, New York, 1976), references cited therein, and H.-D. Beckhaus, C. Rüchardt, S.I. Kozhushkov, V.N. Belov, S.P. Verevkin, and A. de Meijere, *J. Am. Chem. Soc.*, **117**, 11854 (1995).

⁴ J.J.P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989).

⁵ M.R. Ibrahim and P.v.R. Schleyer, *J. Comput. Chem.*, **6**, 157 (1985). A few additional parameters were determined by the present author.

Table (B) Origin of Parameters (Eqns. (5) and (6)) for Reaction-Based Methods by Calculation Level				
Method	$\Delta H_f^\dagger(i')$	$E_{eq}(i)$	$E_{zp}(i)$	$H_{298K}(i)-H_{0K}(i)$
IIC	Exp/G2	SE	SE _(sc)	Exp/SE _(sc)
IIIC	Exp/G2	HF	SE _(sc)	Exp/SE _(sc)
IVC	Exp/G2	HF	HF _(sc)	Exp/HF _(sc)
VC	Exp/G2	MP2	HF _(sc)	Exp/HF _(sc)

d. Reaction-Based Methods—Class C

The sources of the parameters described in equations (5) and (6) for each of the reaction-based methods are summarized in Table (B). The labels, SE, HF, MP2, and G2 denote calculation by semi-empirical, Hartree-Fock, second-order Møller-Plesset, or G2 methods, respectively. Semi-empirical calculations utilized the MNDO, AM1, and PM3 Hamiltonians, as will be indicated by a parenthetical addition to the method label, and Hartree-Fock and MP2 calculations were performed in the 6-31G(d) basis. The label, Exp, followed by a theoretical level indicates the use of available experimental values, either direct or indirect,⁶ in preference to those of theory and (sc) marks theoretical thermodynamic values for which the vibrational frequencies have been multiplicatively scaled (Hartree-Fock/6-31G(d)-0.89⁷ and semi-empirical: MNDO-0.91, AM1-0.95, PM3-0.97, as determined by the present author by comparison of the zero-point energies of target and non-target molecules with scaled Hartree-Fock values).

4. Computational Considerations

All calculations utilized the serial and parallel versions of the GAMESS computational code⁸ and were performed on IBM RS/6000 workstations at AFRL and tens of nodes of the IBM SP machines at the Maui High Performance Computing Center and the Aeronautical Systems Center, Major Shared Resource Center. The largest *ab initio* calculations involved molecules with no symmetry and 483 basis functions and consumed several node-months on the IBM SP.

Quick turn-around and high through-put are enabled by the extensive parallelization implemented in the program. For example, as compared with sequential mode, one sample MP2 calculation ran with around ninety-percent efficiency on eight nodes.

C. Results and Discussion

1. Molecular Geometries

Hartree-Fock optimization indicates that molecules 1 and 3 have the respective D_{2h} and D_{2d} configurations suggested by chemical intuition and that

⁶ Experimental values from correlation of, J.B. Pedley, R.D. Naylor, S.P. Kirby, *Thermochemical Data of Organic Compounds*, Second Ed., (Chapman-Hall, London, 1986), pp. 89ff.

⁷ J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout, and W.J. Hehre, *Int. J. Quantum Chem.: Quantum Chem. Symp.*, **15**, 269 (1981).

⁸ M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery, Jr., *J. Comput. Chem.*, **14**, 1347 (1993).

these minima constitute the only thermodynamically relevant geometries. In contrast, molecule 2 seems to have no symmetry and the Hartree-Fock potential energy surface exhibits three degenerate pairs of closely lying (within ~ 1 kcal/mol) enantiomeric minima. This is expected to modestly degrade the quality of the thermodynamic predictions reported herein, as they assume a single harmonic minimum.

The four remaining compounds were initially subjected to an optimization constrained by D_{2d} symmetry with, on each end of the molecule, the nitrogen-containing groups directed away from one another and the distal methylene hydrogens eclipsed after the manner of propane. Although computation of the full Hessian revealed only real frequencies for one of the molecules, the remaining three had "imaginary frequencies" (magnitude $\leq 34 \text{ cm}^{-1}$) indicating that these are not equilibrium, minimum-energy structures. By sampling a number of geometries resulting from rotation about the distal C-C and C-N bonds, for each molecule an almost degenerate pair of "constrained minima" of D_2 and S_4 symmetry were found to have an energy fully 4 to 7 kcal/mol below the corresponding D_{2d} structures. However, vibrational analysis indicated that each was not a local minimum on the full potential energy surface. Only by allowing non-planarity in the spiro-linked cyclobutane rings (as in cyclobutane itself) were true local minima discovered. A number of combinations of physically justifiable ring-bending distortions starting from both the D_2 and S_4 geometries were sampled and several nearly iso-energetic minima were elucidated. For each molecule the most stable geometries have no symmetry and lie fully 5 to 11 kcal/mol below the D_{2d} -constrained optima. The principal hope that these indeed constitute global minima rests upon the progressive diminution of the stabilization energy with each successive type of distortion from D_{2d} and the extensive, but admittedly not exhaustive, sampling of the alternatives. In any case, deficiencies in the thermodynamic predictions due to the presence of multiple, low-lying minima and an anharmonic, relatively flat potential energy surface are again likely to be manifest.

2. Enthalpies of Formation

Calculated heats of formation for both target and non-target molecules are presented in Tables (C)-(E). For the first two classes of methods, those limited to a single molecule (A and B), results for the target molecules, Table (C), may be compared with those for the non-target molecules, Table (D). As evidenced by the root-mean-squared deviations from either experimental values (RMS(Exp)) or (in lieu of experimental information) the highest level theoretical predictions (RMS(VC)), the computation-free, *ab lateribus* method of Benson clearly outperforms the other tabulated approaches. This appears to be true, not only for the non-target set containing relatively small and simple systems expected to be well-represented among the reference molecules of parameterized empirical methods, but also for the target compounds as well. Although these latter systems have well-characterized classical chemical structures, they, not unexpectedly, manifest predicted heats of formation with a much stronger overall variance, either by virtue of their size or because of the unique character of their strained binding.

The predicted target heats of formation displayed in Table (E) for the reaction-based methods (class C) indicate that the use of isodesmic reactions









Table (C)					
Target-Molecule ΔH_f^\dagger (kcal/mol) <i>Ab Lateribus</i> (A) and Single-Whole-Molecule (B) Methods					
Molecule	IA	IIB(MNDO)	IIB(AM1)	IIB(PM3)	IIIB
1: 	86.6	61.8	79.9	74.0	83.8
2: 	-8.5	-12.4	-0.4	-5.4	-9.1
3: 	-26.9	-62.0	-36.8	-44.6	-30.2
4: 	320.6	307.3	342.7	306.8	281.1
5: 	-19.8	68.5	1.6	-26.1	-27.4
6: 	354.3	313.8	365.5	316.2	308.7
7: 	13.9	73.3	24.9	-18.1	-1.4
RMS Dev. vs. VC, RMS(VC)	11.9	52.9	23.5	13.2	19.0

Table (D)						
Non-Target-Molecule ΔH_f^\dagger (kcal/mol) <i>Ab Lateribus</i> (A) and Single-Whole-Molecule (B) Methods Compared with Experiment						
Molecule	IA ^a	IIB(MNDO)	IIB(AM1)	IIB(PM3)	IIIB ^a	Exp
CH ₄	-15.3 ^b	-11.9	-8.8	-13.0	-17.0	-17.8 ± 0.1
CH ₃ N ₃		66.4	76.7	69.9	60.7	71.0 ^c
CH ₃ NO ₂		3.3	-9.9	-15.9	-17.9	-17.8 ± 0.1
C ₂ H ₆	-20.4	-19.7	-17.4	-18.1	-20.1	-20.0 ± 0.1
CH ₃ OCH ₃	-43.6	-51.2	-53.2	-48.3	-43.6	-44.0 ± 0.1
CH ₃ CH ₂ CH ₃	-25.3	-24.9	-24.3	-23.6	-25.2	-25.0 ± 0.1
cyclopropane	12.8	11.2	17.8	16.3	13.6	12.7 ± 0.1
C(CH ₃) ₄	-40.3	-24.6	-32.8	-35.8		-40.2 ± 0.2
<i>t</i> -BuOH	-75.1	-64.3	-71.6	-71.3	-68.8	-74.7 ± 0.2
	-17.1	-13.2	-16.3	-21.9	-10.1	-16.3 ± 0.3
RMS(Exp)	1.0	9.6	6.0	3.6	4.5	

^a Absent results constitute the sole value in a parameter reference set and so are identical to the experiment by definition.

^b From bond additivity rules.

^c G2 theoretical result from: D.W. Rogers and F.J. McLafferty, *J. Chem. Phys.*, **103**, 8302 (1995).

tends to increase the quality of the results obtained using a given calculational level. Further, none of the methods, including the next most sophisticated requiring the rather expensive Hartree-Fock optimum geometry and Hessian, significantly out-performs the Benson *ab lateribus* method. In addition, it will be noted that the method labeled IIC(PM3) seems roughly competitive with the Benson rules. Although this computationally economical semi-empirical method

does require more human effort, it may be useful in cases in which suitable *ab lateribus* parameters are not available. Its utility for systems lacking classical chemical structures certainly bears further examination.

It must be conceded, however, that all characterizations of target-molecule results, heretofore, rest upon the assumption that the most expensive method, VC (or, in conventional notation, MP2/6-31G(d)//HF/6-31G(d)), closely, or at least best, represents experiment. In a similar study⁹ of a variety of strained hydrocarbons of the type which provide the framework of the target molecules, it was found that methods essentially identical to those here labeled IVC (or HF/6-31G(d)//HF/6-31G(d)) and VC predicted isodesmic heats of formation with RMS deviations from experiment of 10.4 and 2.1 kcal/mol, respectively. These values seem at least consistent with the 11.7 kcal/mol deviation of the IVC results from those of the highest level. Further, it has been found¹⁰ in a different test set that electron-correlation treatments of a sophistication just beyond the MP2 can, in fact, lead to reaction energies of reduced accuracy. In any case, until experimental values or significant additional computational resources become available, the current results would seem to provide the best measure of target-molecule formation enthalpies.

Table (E)						
Target-Molecule ΔH_f^\ddagger (kcal/mol) by Reaction-Based Methods (C)						
Molecule	IIC(MNDO)	IIC(AM1)	IIC(PM3)	IIC(PM3) ^a	IVC	VC
1	61.4	70.8	82.1	82.5	75.1	76.5
2	-19.7	-9.0	-12.2	-9.9	-9.9	-10.2
3	-45.1	3.3	-25.4	-27.4	-29.8	-28.8
4	318.9	362.3	332.5	333.9 ^b	329.3	315.8
5	-22.4	12.9	-12.5	-15.7 ^b	-18.8	-34.7
6	312.0	400.2	348.0	365.0 ^b	358.0	342.7
7	-31.0	51.2	1.5	13.7 ^b	8.4	-8.6
RMS(VC)	17.7	42.0	11.6	15.7	11.7	

^a For brevity only IIC(PM3) results are provided. See, J.D. Mills, *Technical Report*, in preparation, for IIC(MNDO) and IIC(AM1) values.

^b Optimized, semi-empirical structure differs qualitatively from the Hartree-Fock. Thermodynamic parameters are calculated for the local-minimum geometry most resembling the Hartree-Fock.

3. Specific Impulse








The implications of the theoretical results for actual propellant performance may be illuminated in a number of ways. Most simply, a candidate's mass-normalized energy content seems a more appropriate measure of its lifting capability than the common molar value; mass-adjusted heats of formation for the highest level theoretical results are given in Table (F). Further, calculation¹¹ of

⁹ R.L. Disch, J.M. Schulman, M.L. Sabio, *J. Am. Chem. Soc.*, **107**, 1904 (1985).

¹⁰ J.R. Van Wazer, V. Kellö, B.A. Hess, Jr., and C.S. Ewig, *J. Phys. Chem.*, **94**, 5694 (1990).

¹¹ C. Selph, R. Hall, C. Beckman, R. Acree, T. Magee, "Theoretical ISP Code," *Computer Program*, Phillips Lab., Edwards AFB, CA.

the specific impulse, I_{sp} ,¹² provides a more direct measure of the probable utility of a prospective fuel. Even though the target molecules are envisioned as solid- or liquid-propellant additives, the present study does not address the energetics or properties of their condensed phases. Therefore, Table (F) is limited to the specific impulse of each fuel as a gas combusted with liquid oxygen under fixed reference conditions.¹³ It was hoped that these values would provide at least a relative measure of likely performance; under the same conditions, RP-1, a common, kerosene-based hydrocarbon fuel, has a theoretical specific impulse of 299.8 sec.

Table (F) Target-Molecule, Mass-Based Enthalpies of Formation (Method VC) and Specific Impulse		
Molecule	ΔH_f^\dagger (cal/g)	I_{sp} (sec)
1: 	955	313.2
2:  HO	-104	300.7
3: 	-288	295.5
4: 	998	301.6
5: 	-104	287.8
6: 	864	301.8
7: 	-21	292.4

Somewhat surprisingly, the majority of the proposed fuels seem to manifest relatively poor performance or only modest performance gains compared to RP-1. Additional calculations¹⁴ reveal that their specific impulses even show a generally disappointing relationship with those of the non-target isodesmic counterparts—molecules which might be characterized as containing the same functional groups as, but, for the most part, lacking the energy-bestowing strain of, the targets. It was initially supposed that the relatively unsaturated target molecules might simply lack sufficient hydrogen to produce significant quantities of favorable, light exhaust products when burned with oxygen alone and that they might therefore manifest a cooperative enhancement with a relatively hydrogen-rich fuel. However, no tripropellant combination of liquid oxygen and a target fuel with either liquid hydrogen or RP-1 leads to any predicted performance increase. (That is, in each case the optimum specific impulse is just that of a binary mixture of oxygen, and whichever of the other two components has the best performance with oxygen alone.) It appears that condensation energetics and densities must be determined, or at least sensibly hypothesized, in advance of optimization of realistic specific formulations in order to more definitively rank these candidates.

¹² G.P. Sutton, *Rocket Propulsion Elements: An Introduction to the Engineering of Rockets*, Sixth Ed., (Wiley, New York, 1992).

¹³ Sea level expansion with 1000 psi chamber pressure.

¹⁴ J.D. Mills, *Technical Report*, in preparation.

D. Conclusions

The accuracies of a series of progressively more expensive and sophisticated theoretical methods for calculating gas-phase enthalpies of formation have been evaluated in a specialized reference set of strained and substituted molecules in an effort to justify means by which valuable experimental and theoretical resources may be more efficiently focussed on candidates of particular promise. It appears that the computation-free, *ab lateribus* Benson prescription based upon correlations with experimental values can be expected to predict the formation enthalpies of these types of molecules with an error on the order of 10 kcal/mol. As an alternative to very lengthy calculations, facile, semi-empirical computation with the PM3 Hamiltonian in conjunction with isodesmic reactions may provide roughly comparable results for the relatively rare systems to which the simpler method can not be applied. After an initial screening with either of these two approaches, it appears that the progressively sophisticated theoretical methods considered here do not yield significant improvements in accuracy, at least until the level at which energies from a Hartree-Fock-optimized vibrational analysis and MP2 single-point-energy calculation (MP2/6-31G(d)//HF/6-31G(d)) are combined in accord with an appropriate isodesmic reaction.

By themselves, theoretical, gas-phase heats of formation constitute parameters determinative of a simple relative specific-impulse ranking of candidate fuels under reference conditions. Nonetheless, condensed-phase properties and more interaction with researchers in propellant formulations appear to be necessary in order to fully actualize the potential of these investigations to support the effort to reduce the time and expense required to develop and deploy propellants capable of higher performance and increased payload.

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